Density-relaxation part of the self energy

In a recent Letter, Öğüt, Chelikowsky and Louie [1] presented an important series of calculations of the effect of quantum confinement on optical gaps in large hydrogen-passivated spherical silicon clusters, by calculating the quasiparticle energies for addition of an electron and of a hole separately, and then the excitonic binding energy. The quasiparticle energies were calculated by what might be termed a ΔLDA approach: within the local-density approximation (LDA), the ground-state total energies of the n-, $n-1$- and $n+1$-electron systems (where n is the number of electrons in the neutral cluster) were calculated, and then the quasiparticle gap was estimated using

$$\epsilon_{\rm g}^{\rm qp} = E_{n+1} + E_{n-1} - 2E_n. \qquad (1)$$

The authors suggest that this expression would be expected to approach the experimental quasiparticle energy gap of bulk silicon (1.2 eV) in the large-cluster limit. They presented a numerical fit of the correction $\epsilon_{\rm g}^{\rm qp} - \epsilon_{\rm g,LDA}^{\rm qp}$, which they stated approached the bulk value of 0.68 eV like $d^{-1.5}$, where $\epsilon_{\rm g,LDA}^{\rm qp}$ is the LDA Kohn-Sham eigenvalue gap and d is the cluster diameter. However, it is known that in the bulk limit Eq. (1) (in the LDA) simply yields the LDA energy gap: the correction is zero. This is because the LDA exchange-correlation energy is an analytic functional of density: the fact that the change in electron density on adding (or subtracting) a single electron is of order $1/n$ allows the changes in the Kohn-Sham eigenvalues and the other ingredients of the energy to be evaluated using perturbation theory, and after a substantial cancellation between terms the stated result is obtained. (The same formula yields the *correct* gap in exact Kohn-Sham DFT, but this reflects a non-analytic discontinuity in the exchange-correlation potential between the n- and $n+1$-electron systems [2].)

In physical terms, the ΔLDA approach includes the electrostatic effect of the relaxation of the charge density when an electron is added or subtracted, and the corresponding relaxation in the LDA exchange-correlation potential. In the large-cluster limit, both these effects go to zero, and the non-zero band-gap correction may be calculated using many-body perturbation theory in a suitable approximation (e.g. [3,4]), where the correction to the LDA band gap arises from the differing effects of the non-local self-energy on the states concerned [4].

Furthermore, there is no reason to suppose that this term in the self-energy correction that is excluded in the ΔLDA approach is negligible in the clusters studied. Therefore it is likely that the quasiparticle and optical gaps given in Ref. [1] should be increased by very approximately 0.68 eV, where the error bar in this estimated correction is smallest for the largest clusters. Of course, this additional correction is of lower relative importance for the smaller clusters.

To confirm our theoretical analysis, we have reanalyzed the data for the ΔLDA gap correction from Ref. [1], shown here in Fig. 1 as a function of $1/d$. The dashed curve shows the best (least-squares) fit of the form 0.68 eV + Ad^{-p}, as in Ref. [1], obtained by us with p =1.40 (similar to the 1.5 given in Ref. [1]). The solid curve shows the best fit obtained if the constraint that the limit as $d \to \infty$ should be 0.68 eV is removed (as it should be): $K + Ad^{-p}$ with K=(0.12±0.24) eV, $p = 0.92 \pm 0.14$. The value of K is indeed consistent with zero, and inconsistent with 0.68 eV. The second fit is more than twice as good as the first, as measured by χ^2.

R.W. Godby[a], and I.D. White[b]

[a]Department of Physics, University of York, Heslington, York YO1 5DD, U.K.

[b]Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, U.K.

[1] Serdar Öğüt, James R. Chelikowsky and Steven G. Louie, Phys. Rev. Lett. **79**, 1770 (1997).

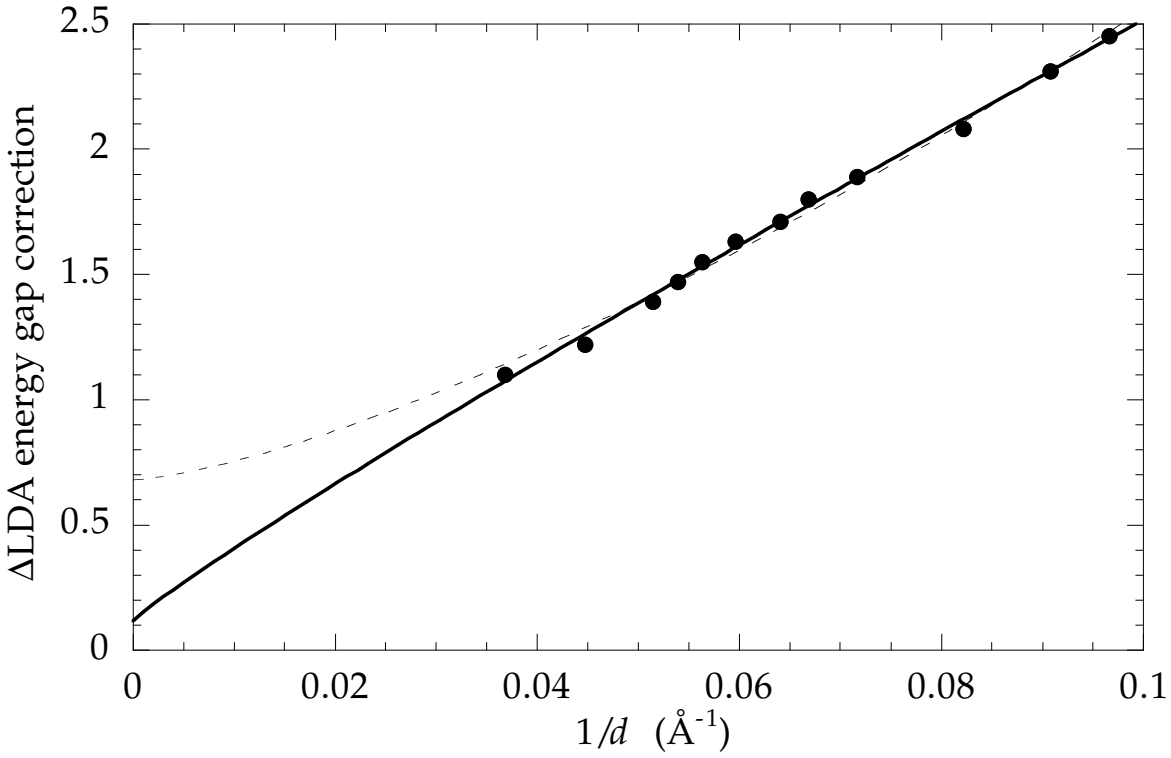
[2] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983), J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[3] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985).

[4] R. W. Godby, M. Schlüter and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

FIGURE CAPTIONS

Fig.1 The band-gap correction from Ref. [1], plotted against the inverse cluster diameter. The best fit (solid curve) correctly tends to a value consistent with zero.


2.5
2
1.5
1
0.5
0
ΔLDA energy gap correction
0
0.02
0.04
0.06
0.08
0.1
1/d (Å-1)